Title: **EP1035179A1: Ink-jet printing ink compositions having superior smear-fastness** [German] [French]

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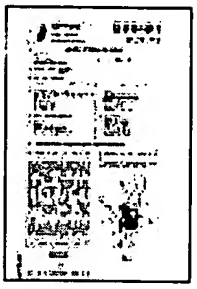

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Assignee: **Hewlett-Packard Company**
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Abstract:

Specific core-shell, or latex, binders and additives for use in ink-jet printing ink compositions are provided. One class of specific core/shell binders has the general formula [AmBnC'p,Fs]x, where A and B are hydrophobic components in which A exhibits a glass transition temperature Tg between about -150° and +25°C and B exhibits a glass transition temperature greater than 25°C, C' is a component that forms a hydrophilic or water-soluble component in the polymer chain, and has an ionic or non-ionic structure, F contains oxygen-hydrogen functional groups such as aldehydes, carboxylic acids, allyl alcohols, acetals, and hemiacetals, m < 30 wt%, n >40 wt%, p < 30 wt%, and s < 30 wt%, with the total of m + n + p + s = 100 wt%, and x = 1 to 100,000. The molecular weight (weight average) of the polymer is between about 1,000 and 2,000,000. The polymers useful in the practice of the invention are prepared by emulsifying the monomers and then conducting a free-radical polymerization in water. The foregoing binder polymer is used in conjunction with amine-containing additives comprising either (a) amine alcohols having the general formula where R1 and R2 are independently selected from the group consisting of hydrogen, alkyl, alkoxy, aryl, and phenoxy, R is alkyl, X is selected from the group consisting of hydrogen, alkyl, aryl, -OH, -COOH, -CHO, and substituted groups; (b) amines, or (c) polyamines. In the ink compositions of the present invention, the ratio of binder (I) to colorant (pigment) is greater than 1 to 10. The concentration of the amine-containing additive in the ink is within the range of 0.01 to 10 wt%.

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INPADOC Legal Status: Show legal status actions Get N w: Family Legal Status Report

Designated Country: AL AT BE CH CY DE DK ES FI FR GB GR IE IT LI LT LU LV MC MK NL PT RO SE SI

Family:

PDF	Publication	Pub. Date	Filed	Title
☑	JP2000290567A2	2000-10-17	2000-03-09	INK COMPOSITION FOR INK JET PRINTING EXCELLENT IN COLOR FASTNESS TO STAIN
☑	JP0290567A2	2000-10-17	2000-03-09	
☒	**EP1035179A1**	2000-09-13	2000-02-22	Ink-jet printing ink compositions having superior smear-fastness
3 family members shown above				

Description: Expand full description

First Claim: Show all claims

1. An ink-jet printing ink composition comprising a vehicle and a colorant, wherein said composition further includes at least one latex polymeric binder to increase smearfastness of said composition and an amine-containing additive to said vehicle, said latex polymeric binder having a formula given by

wherein *A*, *B*, *C*, *D*, *E*, and *F* are moieties as follows:

- *D* = at least one UV absorber;
- *E* = at least one moiety having at least one highly polar functional group;
- *F* = a moiety having at least one functional group selected from aldehydes, carboxylic acids, allyl alcohols, acetals, and hemiacetals;
- m = 10 to 90 wt%;
- n = 10 to 90 wt;
- p = 0 to 60 wt%;
- q = 0 to 50 wt%;
- r = 0 to 40 wt%;
- s = 1 to 30;
- m + n + p + q + r + s = 100 wt%; and
- x = 1 to 100,000,

wherein said polymer has either hydrophobic and hydrophilic moieties or has only hydrophobic moieties and is associated with said surfactant to form a polymer/surfactant system, said polymer or polymer/surfactant system capable of forming a film from water, which, upon dehydration, is essentially resistant to water, said polymer having a T_g within the range of about -10° to +110°C, said amine-containing additive consisting essentially of a water-soluble or water-dispersible amine, polyamine, or amine alcohol, said amine alcohol having a formula given by where R_1 and R_2 are independently selected from the group consisting of hydrogen, alkyl, alkoxy, aryl, and phenoxy, R is alkyl, X is hydrogen, alkyl, aryl, -OH, -COOH, and -CHO.

Forward References:

Go to Result Set: Forward references (1)

PDF	Patent	Pub.Date	Inventor	Assignee	Title
	US6610412	2003-08-26	Ungefug; Gary Allan	Hewlett-Packard Development Company, L.P.	Printing fluid additives promoting overcoat adhesion

Other Abstract Info:

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(54) Ink-jet printing ink compositions having superior smear-fastness

(57) Specific core-shell, or latex, binders and additives for use in ink-jet printing ink compositions are provided. One class of specific core/shell binders has the general formula $[A_mB_nC'_pF_s]_x$, where A and B are hydrophobic components in which A exhibits a glass transition temperature T_g between about -150° and +25°C and B exhibits a glass transition temperature greater than 25°C, C' is a component that forms a hydrophilic or water-soluble component in the polymer chain, and has an ionic or non-ionic structure, F contains oxygen-hydrogen functional groups such as aldehydes, carboxylic acids, allyl alcohols, acetals, and hemiacetals, m < 30 wt%, n >40 wt%, p < 30 wt%, and s < 30 wt%, with the total of m + n + p + s = 100 wt%, and x = 1 to 100,000. The molecular weight (weight average) of the polymer is between about 1,000 and 2,000,000. The polymers useful in the practice of the invention are prepared by emulsifying the monomers and then conducting a free-radical polymerization in water. The foregoing binder polymer is used in conjunction with amine-containing additives comprising either (a) amine alcohols having the general formula

$$R_1R_2N(R)\text{-}OH,$$
$$|$$
$$X$$

where R_1 and R_2 are independently selected from the group consisting of hydrogen, alkyl, alkoxy, aryl, and phenoxy, R is alkyl, X is selected from the group consisting of hydrogen, alkyl, aryl, -OH, -COOH, -CHO, and substituted groups; (b) amines, or (c) polyamines. In the ink compositions of the present invention, the ratio of binder (I) to colorant (pigment) is greater than 1 to 10. The concentration of the amine-containing additive in the ink is within the range of 0.01 to 10 wt%.

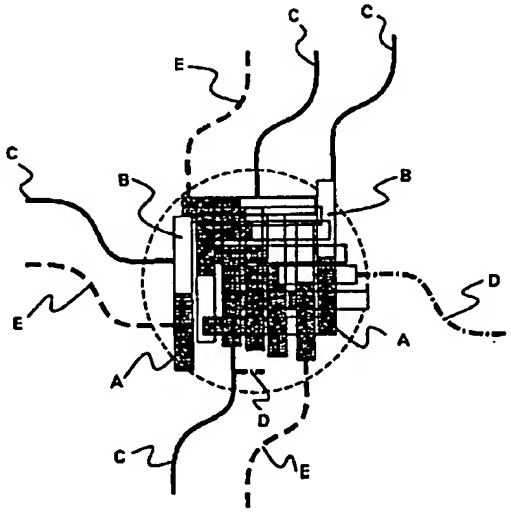


FIG.1

EP 1 035 179 A1

Description

CROSS-REFERENCE TO RELATED APPLICATION

[0001] The present application is a continuation-in-part of application Serial Number 08/998,164, filed December 24, 1997, which is a continuation-in-part of application Serial Number 08/962,496, filed October 31, 1997. That application is directed to core/shell polymers in general for use in a variety of applications, including ink-jet printing inks. The present application is directed to a specific class of such core/shell polymers for use in ink-jet printing inks. The present application is also related to application Serial Numbers 09/120,046, filed July 21, 1998, 09/120,270, filed July 21, 1998, and 09/138,772, filed August 24, 1998.

TECHNICAL FIELD

[0002] The present invention relates generally to ink-jet printing ink compositions having superior smearfastness, as compared to prior art ink-jet ink printing compositions, and, more particularly, to the use of core/shell and other polymers, or binders, with hydrophobic and hydrophilic portions that contribute to such superior smearfastness and additives to the inks that improve their print reliability.

BACKGROUND ART

[0003] Core/shell polymers are well-known; such polymers typically have a hydrophilic portion and a hydrophobic portion comprising a latex particle morphology consisting of an inner "core", surrounded by an outer "shell". Core/shell polymers are commonly used to disperse molecules or particles, such as pigments, which are ordinarily insoluble in water, but which, after association with the core/shell polymer, form stable dispersions in water. Dispersion occurs when the hydrophobic portion of the polymer associates with the water-insoluble molecule or particle, and the hydrophilic portion of the polymer disperses with water.

[0004] U.S. Patent 4,597,794 discloses the dispersion of pigments in an aqueous vehicle, using aqueous binders comprising both hydrophilic and hydrophobic components. The dispersion of the pigment is followed by centrifugation to eliminate the non-dispersed components such as agglomerates. Examples of the hydrophilic component comprise polymers of monomers having a mainly additively polymerizable vinyl group, into which hydrophilic construction portions such as carboxylic acid groups, sulfonic acid groups, sulfate groups, etc. are introduced by using a predetermined amount of an α,β-unsaturated monomer such as acrylic acid, methacrylic acid, crotonic acid, itaconic acid, itaconic acid monoester, maleic acid, maleic acid monoester, fumaric acid, fumaric acid monoester, vinyl sulfonic acid, sulfoethyl methacrylate, sulfopropyl methacrylate, sulfonated vinylnaphthalene, etc. Examples of the hydrophobic portion comprise polymers of monomers selected from the group consisting of styrene, styrene derivatives, vinylnaphthalene, vinylnaphthalene derivatives, and α,β-ethylenic unsaturated carboxylate of aliphatic alcohol having C_8-C_{18}. In addition to the foregoing monomers, also included are acrylonitrile, vinylidene chloride, α,β-ethylenic unsaturated carboxylate, vinyl acetate, vinyl chloride, acrylamide, methacrylamide, hydroxyethyl methacrylate, hydroxypropyl methacrylate, glycidyl methacrylate, N-methylol acrylamide, N-butoxymethyl acrylamide, etc.

[0005] U.S. Patent 5,082,757 discloses encapsulated toner compositions comprising a core and a hydroxylated polyurethane microcapsule shell derived from the polycondensation of a polyisocyanate and a water soluble carbohydrate. The core comprises a polymer binder, pigment, dye, or mixtures thereof. Examples of the polymer binder include polymerized monomers selected from the group consisting of acrylates, methacrylates, and olefins including styrene and its derivatives.

[0006] U.S. Patent 5,461,125 discloses waterborne core-shell latex polymers useful as adhesive films, rather than super-dispersion stability. The core comprises a (co)polymer comprising a (meth)acrylate ester, while the shell comprises a copolymer, the copolymer comprising (1) a nitrogen-bearing ethylenically-unsaturated free-radically polymerizable monomer, (2) at least one (meth)acrylate ester of about a C_1 to C_{14} alcohol, and (3) an optional ethylenically-unsaturated free-radically polymerizable silane monomer, wherein the nitrogen-bearing ethylenically-unsaturated free-radically polymerizable monomer comprises about 15 to 60 wt% of the shell and wherein the core comprises about 40 to 85 wt% of the weight of the total core-shell latex particle. The polymers obtained by practicing the teachings of the disclosure have molecular weights of 400,000 or more, and the total low T_g component (less than -10°C), where T_g is the glass transition temperature, is greater than 60 wt%.

[0007] U.S. Patent 5,656,071 discloses ink compositions useful for ink-jet applications. These compositions include an insoluble pigment and a polymeric dispersant. In one embodiment, the polymeric dispersant comprises block or graft copolymers comprising a hydrophilic polymeric segment (particularly an acrylate or methacrylate copolymer) and a hydrophobic polymeric segment which includes a hydrolytically stable siloxyl substituent.

[0008] Heretofore, ink-jet printers have not had printing performance and durable print properties of competitive

printer technologies. The foregoing cited patents do not provide for useful, durable film-forming properties upon removal of the water or solvent. Film durability includes wet and dry rub resistance, highlighter smearfastness, lightfastness, and waterfastness (e.g., hot and cold water, under spill, soak, and rub conditions).

[0009] In particular, formulating an ink-jet ink often involves compromising competing interests. For example, it is possible to enhance one property, such as durable film-forming of the colorant. However, such enhancement usually results in the degradation of another property, such as printing stability associated in thermal ink-jet with resistor fouling or nozzle clogging (kogation or decap - nozzle crusting).

[0010] Many thermal ink-jet inks exhibit poor smearfastness due to the aqueous solubility of the colorant and/or the dispersibility of the colorant. Efforts continue to develop ink-jet printing ink compositions that evidence the level of smearfastness that a water-insoluble colorant, such as a pigment, possesses, while retaining other desirable printing characteristics.

<u>DISCLOSURE OF INVENTION</u>

[0011] In accordance with the invention, specific latex binders and certain amine-containing vehicle additives for use in ink-jet printing ink compositions are provided. The specific latex binders have the general formula (I)

$$[(A)_m(B)_n(C)_p(D)_q(E)_r(F)_s]_x \qquad (I)$$

wherein *A*, *B*, *C*, *D*, *E*, and *F* represent functionalities as follows:

A = at least one hydrophobic component contributing to improved durable, film-forming properties selected from moieties which, when homo-polymerized to a solid state, have a glass transition temperature (T_g) in the range between -150° and +25°C;
B = at least one hydrophobic and solvent barrier moiety used to adjust the T_g of the hydrophobic component of the polymer (I) which, when homo-polymerized to a solid state, has a T_g greater than +25°C;
C = at least one hydrophilic component, selected from a wide variety of water-soluble monomers (optional);
D = at least one UV absorber (optional);
E = a moiety having at least one highly polar functional group (optional);
F = a moiety having at least one functional group selected from aldehydes (-CHO), carboxylic acids (-COOH), allyl alcohols ($-CH_2OH$), acetals, and hemiacetals;
m = 10 to 90 wt%;
n = 10 to 90 wt%;
p = 0 to 60 wt%;
q = 0 to 50 wt%;
r = 0 to 40 wt%;
s =1 to 30 wt%;
m + n + p + q + r + s = 100 wt% ; and
x = 1 to 100,000,
with the proviso that at least one of *C* and *E* must be present.

[0012] The molecular weight (weight average) of polymer (I) is between about 5,000 and 5,000,000.

[0013] The polymers useful in the practice of the invention are prepared by emulsifying the monomers and then conducting a free-radical polymerization in water.

[0014] The amine-containing vehicles employed in the practice of the present invention include water-soluble or water-dispersive amines, polyamines, and amine alcohols, employed as an additive to the aqueous-based vehicle, which contains one or more water-miscible organic co-solvents. The amine alcohols have the general formula (II)

$$R_1R_2N(R)\text{-}OH \text{ , with X attached to R} \qquad (II)$$

where R_1 and R_2 are independently selected from the group consisting of hydrogen, alkyl, alkoxy, aryl, and phenoxy, R is alkylene, and X is selected from the group consisting of hydrogen, alkyl, aryl, -OH, -COOH, and -CHO.

[0015] The ink formulation of the present invention comprises:

5 to 50 wt% water-miscible solvent;
0.5 to 10 wt% colorant;
0.1 to 10 wt% latex polymeric binder;
0.01 to 10 wt% amine-containing additiv ; and
water.

[0016] The functional groups and amine-containing additives described above chemically react with cellulosic media such as plain papers, textiles, and paper coatings containing cellulosic components. The reactivity is achieved by including moiety *F* above in the latex binder and by including the amine-containing additive in the ink.

[0017] Without subscribing to any particular theory, it appears that the functional groups allow the latex binder to react with cellulosic materials to form a permanent attachment and thus a smearfast ink.

[0018] Employing the latex binder with functional groups as listed above in an aqueous ink permits permanent printing of ink on print media, such as plain paper, textiles, etc., and gives rise to a significant enhancement of smear fastness, especially against highlight markers, which rivals that of a laser or xerographic print. While printing on plain paper may be performed, however, the drying times of the inks may require longer drying times than other ink-jet inks and thus heating elements may be necessary. On the other hand; printing on textiles, such as cotton T-shirts, eliminates printing first on a transfer medium, which is then printed onto the fabric. Instead, the inks of the present invention permit direct printing onto the fabric, and the printed ink is fixed on the fabric by a heating means, such as a hot iron.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] The sole Figure is a schematic diagram of the film-forming, water-dispersive polymer used in the practice of the present invention.

BEST MODES FOR CARRYING OUT THE INVENTION

Definitions

[0020] The following definitions are made:

[0021] The term "core/shell polymer" means a water-dispersive polymer comprised of a solid hydrophobic core surrounded by (either physically or chemically) a water-soluble shell component, or similar polymers of undefined morphology containing a mixture of hydrophobic and hydrophilic groups. This is often referred to herein as a "latex polymer".

[0022] The term "substituted" is meant to include alcohols (OH), esters (COOR), aldehydes (CHO), carboxylic acids (COOH), thiols (SH), amino groups (NH_2, NHR, NR_2) nitro group (NO_2), nitriles (CN), isocyanides (NC), cyanates (CNO), isocyanates (NCO), amido groups, epoxies, halogens, siloxanes, and pyrridinyls. The term "halogen" is meant to include fluorine, chlorine, bromine, and iodine.

[0023] All concentrations are given in terms of weight percent (wt%), unless otherwise specified. All values of molecular weight of polymers are given in terms of weight average.

Monomeric Moieties

[0024] In accordance with the present invention, latex binders have the following general structure given by formula (I)

$$[(A)_m(B)_n(C)_p(D)_q(E)_r(F)_s]_x \qquad (I)$$

wherein *A*, *B*, *C*, *D*, *E*, and *F* represent functionalities as follows:

A = at least one hydrophobic component contributing to improved durable, film-forming properties selected from moieties which, when homo-polymerized to a solid state, have a glass transition temperature (T_g) in the range between -150° and +25°C, preferably -100° to +10°C, more preferably from -60° to +0°C;
B = at least one hydrophobic and solvent barrier moiety used to adjust the T_g of the hydrophobic component of the polymer (I) which, when homopolymerized to a solid state, has a T_g greater than +25°C;
C = at least one hydrophilic component, selected from a wide variety of water-soluble monomers (optional);
D = at least one UV absorber (optional);
E = a moiety having at least one highly polar functional group (optional);
F = a moiety having at least one functional group selected from aldehydes (-CHO), carboxylic acids (-COOH), allyl alcohols ($-CH_2OH$), acetals, and hemiacetals;

m = 10 to 90 wt%;
n = 10 to 90 wt%;
p = 0 to 60 wt%;
q = 0 to 50 wt%;
r = 0 to 40 wt%;
s = 1 to 30 wt%;
m + n + p + q + r + s = 100 wt% ; and
x = 1 to 100,000,
with the proviso that at least one of *C* and *E* must be present.

[0025] Preferably, the latex polymer has the structure given by formula (I')

$$A_x B_y C'_z F_w \qquad (I')$$

where A, B and F are as defined above, C' is either C or E or both C and E, x < 30 wt%, y > 40 wt%, z < 30 wt%, and w < 30 wt%.

[0026] The molecular weight (weight average) of polymer (I) or (I') is between about 1,000 and 2,000,000, preferably between about 5,000 and 500,000, and most preferably between about 10,000 and 70,000.

[0027] Preferably, the final T_g of the polymer(s) (I) or (I') is within the range of about -25° to +110°C, and more preferably, the final T_g is within the range of about -15° to +90°C, and most preferably within the range of about -10° to +75°C.

[0028] The polymer (I) or (I') is designed to have both hydrophobic and hydrophilic moieties. Thus, the polymer is both (1) water-dispersible, and includes water-soluble polar groups, which are present in sufficient quantity to suspend a pigment particle, and (2) hydrophobic, with a substantial fraction of the polymer containing hydrophobic moieties that are either highly water-resistant or even water-insoluble.

[0029] The hydrophobic *A* moiety allows the polymer to have a sufficiently low T_g to permit formation of a film with other polymer molecules containing the A moiety. The film formation results upon drying (removal of water).

[0030] The hydrophobic *B* moiety in combination with the hydrophobic A moiety provides the polymer with resistance to environmental solvents, such as water and those found in highlighter pens. Additional environmental solvents can be found in rain, coffee, soda pop, body oils, soils, hot water, etc.

[0031] The hydrophilic *C* moiety may be provided in the polymer itself, as shown in formula (I). At least one *C* moiety may be present, and is water-soluble. If present, such water-soluble moieties comprise an ionic or non-ionic shell of the core-shell polymer. Alternatively, the *C* moiety may be provided by one or more surfactants, to form a polymer/surfactant system. Any of the ionic (anionic and cationic), non-ionic, and zwitterionic (amphoteric) surfactants may be employed. A representative listing of applicable surfactant can be found in McCutcheon's Emulsifiers and Detergents, North American Edition, 1997, McCutcheon's Division, MC Publishing Co. 175 Rock road, Glen Rock, NJ 07452 USA Examples of surfactants that may be beneficially employed in the practice of the present invention include: TERGITOLs, which are polyethylene or polypropylene oxide ethers; alkyl phenyl polyethylene oxides available under the tradenane TRITONs, ; BRIJs, which are polyethylene or polypropylene oxide ethers; PLURONICs, which are also polyethylene/o polypropylene oxide copolymers from BASF; and the SURFYNOLs, which are acetylenic ethoxylated diols; polyethylene oxide (POE) esters; POE diesters; POE amines; protonated POE amines; POE amides; the polypropylene analogs of the foregoing POE compounds; dimethicone copolyols; quaternary ammonium compounds; AEROSOLS, including sulfosuccinates; ethoxylates, amine oxides, and betaines.

[0032] Preferred examples of non-ionic surfactants include, but are not limited to, BRIJs, which are polyethylene oxide ethers, available from ICI Surfactants (specific examples include the following BRIJs: 30, 35, 52, 56, 58, 72, 76, 78, 92, 97, and 98); TWEENs, which are derivatives of polyethylene oxides, available from ICI Surfactants (specific examples include the following TWEENs: 20, 40, 60, 80, and 85); SOLSPERSE 27,000, which is an aromatic ethoxylate, available from Zeneca; SPAN 85, which is available from Air Products; and SURFYNOLs, which are acetylenic ethylene oxides available from Air Products. Examples of anionic surfactants include AEROSOL DPOS 45, which is a sulfate, available from Cytec Industries; sodium octadecyl sulfonate; dioctyl ester of sodium sulfosuccinic acid; AEROSOL OT 100%, which is a sulfate, available from American Cyanamid; and sodium lauryl sulfonate. The preferred surfactants include SURFYNOL 465 and SOLSPERSE 27,000.

[0033] If used, the amount of surfactant ranges from about 0.001 to 30 wt%, and the balance the polymer.

[0034] Optionally, one or more UV absorber moieties *D* may be present. The UV absorber contains a UV blocking chromophore, which imparts lightfastness to the polymer.

[0035] Also optionally, one or more ionic water-soluble, dispersible moieties *E* may be present. If present, such water-soluble moieties comprise an ionic shell of the core-shell polymer.

[0036] Although the *C* and *E* moieties are indicated as being optional, at least one of these two moieties must be

present in the polymer.

[0037] The *F* moiety contains oxygen-hydrogen-containing functional groups which react with cellulose to thereby form a permanent attachment of the core-shell binder in the ink to the cellulose structure. Such permanent attachment renders the printed ink waterfast and smearfast on the cellulosic material.

[0038] One moiety (monomer) may be employed to provide one or more of the foregoing functions. Alternatively, one function may be provided by one or more of the foregoing moieties. However, in many instances, a single moiety provides a single function.

[0039] Typically, the polymer(s) of the present invention is prepared by emulsifying the monomeric components, and then conducting a free-radical polymerization in water. Free-radical polymerization involves employing a free-radical initiator. A concentration of about 0.001 to 10 wt% of the initiator is employed in the total monomer system. Examples of suitable free-radical initiators include, but are not limited to, ammonium persulfate, potassium persulfate, hydrogen peroxide, benzoyl peroxide, azobisisobutyronitrile, TRIGONOX 21, and PERKADOX 16. Preferably, the resulting polymer (I) is a random polymer.

[0040] Two or more moieties (monomers) may be copolymerized. Alternatively, two or more polymers may be blended together.

[0041] One skilled in this art would understand that the polymer(s) can also be prepared by conventional condensation techniques. Once a film is formed from the polymer and water is removed, as by dehydration under ambient conditions, the film is essentially impervious to water, and the polymer is not capable of being redispersed with water. If the polymer or polymer/surfactant system is associated with pigment particles, and the pigment with polymer or polymer/surfactant system is deposited on a surface, such as paper, then the pigment particles are trapped within or beneath the film on the surface, and are thus protected from the effects of water and environmental solvents.

[0042] The sole Figure illustrates a molecule of polymer (I). Moieties *A* and *B* form a solid core. The *C* moiety forms a non-ionic, water-soluble shell. The *D* moiety is a UV absorber. The *E* moiety forms an ionic, water-soluble or water-insoluble shell. The *F* moiety (not shown) forms either a water-soluble shell if it is a short chain or is part of the core if it is a long alkyl chain.

[0043] As stated above, the *A* moiety is a hydrophobic component for controlling solubility in organic solvents selected from monomer(s) that form homopolyers having a T_g in the range between -150° and +25°C. The *A* moiety is preferably selected from ethylenically-substituted compounds given by (A):

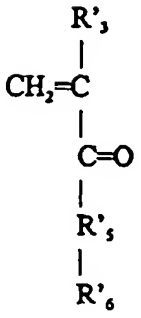
$$C(R_1)(R_2)=C(R_3)R_4R_5R_6 \qquad (A)$$

where

R_1 and R_2 are independently hydrogen, halogen, alkyl, aryl, or substituted alkyl or aryl, or vinyl butyral,
R_3 is hydrogen, halogen, saturated or unsaturated alkyl, alkoxy, aryl, or substituted alkyl, alkoxy, or aryl,
R_4 is direct bond, O, CO, NH, halogen, saturated or unsaturated alkyl, aryl, or substituted alkyl, aryl, or CN,
R_5 is absent (if R_4 is alkyl, aryl, or substituted alkyl or aryl or halogen), direct bond, hydrogen, NH, O, alkyl, alkylene, aryl, or substituted alkyl, alkylene, or aryl, and
R_6 is absent (if R_4 is alkyl, aryl, or substituted alkyl or aryl or halogen or if R_5 is hydrogen, alkyl, aryl, or substituted alkyl or aryl), NH_2, saturated or unsaturated alkyl, alkoxy, aryl, aroxy, or substituted alkyl, or aryl.

[0044] The alkyl, alkoxy, alkylene, and aryl chains each contain more than one carbon atom and less than 40 carbon atoms. Preferably, the R_4 functionality is an electron acceptor moiety.

[0045] One preferred embodiment of formula (A) is the following general structure (A1):



(A1)

where

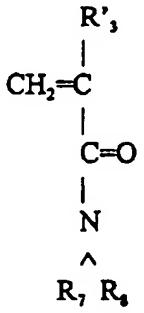
R'_3 = H, halogen, alkyl, aryl or substituted alkyl or aryl;
R'_5 = direct bond, O, or NH; and
R'_6 = alkyl, substituted alkyl, alkylaryl or substituted alkylaryl and aralkyl in which the length of alkyl, alkylaryl or aralkyl chain is given as the number of C atoms between 2 and 40; and alkyl or aryl siloxanes.

[0046] Examples for structure (A1) include, but are not limited to:

(A1-1) ethyl acrylate;
(A1-2) ethyl methacrylate;
(A1-3) benzyl acrylate;
(A1-4) benzyl methacrylate;
(A1-5) propyl acrylate;
(A1-6) propyl methacrylate;
(A1-7) iso-propyl acrylate;
(A1-8) iso-propyl methacrylate;
(A1-9) butyl acrylate;
(A1-10) butyl methacrylate;
(A1-11) hexyl acrylate;
(A1-12) hexyl methacrylate;
(A1-13) octadecyl methacrylate;
(A1-14) octadecyl acrylate;
(A1-15) lauryl methacrylate;
(A1-16) lauryl acrylate;
(A1-17) hydroxyethyl acrylate;
(A1-18) hydroxyethyl methacrylate;
(A1-19) hydroxyhexyl acrylate;
(A1-20) hydroxyhexyl methacrylate;
(A1-21) hydroxyoctadecyl acrylate;
(A1-22) hydroxyoctadecyl methacrylate;
(A1-23) hydroxylauryl methacrylate;
(A1-24) hydroxylauryl acrylate;
(A1-25) phenethyl acrylate;
(A1-26) phenethyl methacrylate;
(A1-27) 6-phenylhexyl acrylate;
(A1-28) 6-phenylhexyl methacrylate;
(A1-29) phenyllauryl acrylate;
(A1-30) phenyllauryl methacrylate;
(A1-31) 3-nitrophenyl-6-hexyl methacrylate;
(A1-32) 3-nitrophenyl-18-octadecyl acrylate;
(A1-33) ethyleneglycol dicyclopentyl ether acrylate;
(A1-34) vinyl ethyl ketone;

(A1-35) vinyl propyl ketone;
(A1-36) vinyl hexyl ketone;
(A1-37) vinyl octyl ketone;
(A1-38) vinyl butyl ketone;
(A1-39) cyclohexyl acrylate;
(A1-40) 3-methacryloxypropyldimethylmethoxysilane;
(A1-41) 3-methacryloxypropylmethyldimethoxysilane;
(A1-42) 3-methacryloxypropylpentamethyldisiloxane;
(A1-43) 3-methacryloxypropyltris(trimethylsiloxy)silane;
(A1-44) 3-acryloxypropyldimethylmethoxysilane;
(A1-45) acryloxypropylmethyldimethoxysilane;
(A1-46) trifluoromethyl styrene;
(A1-47) trifluoromethyl acrylate;
(A1-48) trifluoromethyl methacrylate;
(A1-49) tetrafluoropropyl acrylate;
(A1-50) tetrafluoropropyl methacrylate;
(A1-51) heptafluorobutyl methacrylate;
(A1-52) iso-butyl acrylate;
(A1-53) iso-butyl methacrylate;
(A1-54) 2-ethylhexyl acrylate;
(A1-55) 2-ethylhexyl methacrylate;
(A1-56) iso-octyl acrylate; and
(A1-57) iso-octyl methacrylate.

[0047] Another preferred embodiment for formula (A) is the following general structure (A2):



(A2)

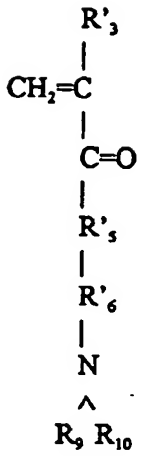
where

R'_3 = same definition as that of structure (A1) above; and
R_7 = R_8 = same or different combinations of R'_6 in structure (A1) above.

[0048] An example for structure (A2) includes, but is not limited to:

(A2-1) N,N-dihexyl acrylamide; and
(A2-2) N,N-dioctyl acrylamide.

[0049] Yet another preferred embodiment for formula (A) is the following general structure (A3):



(A3)

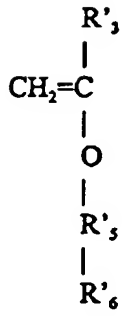
where

R'_3 = same definition as that of structure (A1);
R'_5 = same definition as that of structure (A1);
R'_6 = alkylene, arylene, substituted alkylene or arylene; and
R_9 and R_{10} are independently selected from H, alkyl, substituted alkyl, alkylaryl or substituted alkylaryl in which the length of alkyl and alkylaryl chains each comprise between 2 and 40 C atoms. Alternatively, R_9 and R_{10} together may form a 5-or 6-membered ring.

[0050] Examples for structure (A3) include, but are not limited to:

(A3-1) aminoethyl acrylate;
(A3-2) aminopropyl acrylate;
(A3-3) aminopropyl methacrylate;
(A3-4) aminoisopropyl acrylate;
(A3-5) aminoisopropyl methacrylate;
(A3-6) aminobutyl acrylate;
(A3-7) aminobutyl methacrylate;
(A3-8) aminohexyl acrylate;
(A3-9) aminohexyl methacrylate;
(A3-10) aminooctadecyl methacrylate;
(A3-11) aminooctadecyl acrylate;
(A3-12) aminolauryl methacrylate;
(A3-13) aminolauryl acrylate;
(A3-14) N,N-dimethylaminoethyl acrylate;
(A3-15) N,N-dimethylaminoethyl methacrylate;
(A3-16) N,N-diethylaminoethyl acrylate;
(A3-17) N,N-diethylaminoethyl methacrylate; and
(A3-18) piperidino-N-ethyl acrylate.

[0051] Still another preferred embodiment for formula (A) is the following general structure (A4):



(A4)

where:

R'_4 = H, halogen, alkyl, aryl, sustituted alkyl or aryl;
R'_5 = direct bond, CO, alkylene, arylene, substituted alkylene or arylene; and
R'_6 = alkyl, aryl, substituted alkyl or aryl.

[0052] Examples for structure (A4) include, but are not limited to:

(A4-1) vinyl propionate;
(A4-2) vinyl acetate;
(A4-3) vinyl butyrate;
(A4-4) vinyl butyl ether; and
(A4-5) vinyl propyl ether.

[0053] As stated above, the B moiety is hydrophobic and is a solvent barrier composed of monomer(s) that form homopolymers having a T_g greater than 25°C. The B moiety has the general structure given by formula (B)

$$CR_1R_2=C(R_3)R''_4R''_5R''_6 \quad (B)$$

where

R_1 and R_2 are independently hydrogen, halogen, or vinyl butyral,
R_3 is hydrogen, halogen, saturated or unsaturated alkyl, alkoxy, aryl, or substituted alkyi, aikoxy, or aryl,
R''_4 is direct bond, O, CO, NH, halogen, saturated or unsaturated alkyl, aryl, or substituted alkyl, aryl, or CN,
R''_5 is absent (if R_4 is alkyl, aryl, or substituted alkyl or aryl or halogen), direct bond, hydrogen, NH, O, alkyl, alkylene, aryl, or substituted alkyl, alkylene, or aryl, and
R''_6 is absent (if R_4 is alkyl, aryl, or substituted alkyl or aryl or halogen or if R_5 is hydrogen, alkyl, aryl, or substituted alkyl or aryl), NH_2, saturated or unsaturated alkyl, alkoxy, aryl, aroxy, or substituted alkyl or aryl.

[0054] The alkyl, alkoxy, alkylene, aryl, aroxy chains each contain from 1 to 40 carbon atoms. Additionally, R_1 and R_2 and R_2 and R_3 can each form a ring; one example of a ring compound so formed includes, but is not limited to, polyvinyl butryal. Further, R''_4 and R_5 can form a ring through either nitrogen or oxygen.

[0055] Formula (B) is seen to be substantially the same as formula (A), but with some differences in the substituent groups, which provide a homopolymer of these monomers with the higher T_g of at least 25°C.

[0056] One preferred embodiment of formula (B) is the following general structure (B1):

$$CH_2=CR'''_5R'''_6 \quad (B1)$$

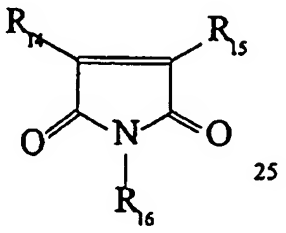
where

R'''_5 = hydrogen, alkyl, alkoxy, aryl or halogen; and
R'''_6 = H, aryl, alkyl (with one carbon atom), amino, ester, epoxy component containing groups, and fluoroalkyl derivatives.

[0057] Examples for formula (B1) include, but are not limited to;

(B1-1) ethylene;
(B1-2) styrene;
(B1-3) vinyl carbazole;
(B1-4) vinyl naphthalalene;
(B1-5) vinyl anthracene;
(B1-6) vinyl pyrene;
(B1-7) methyl methacrylate;
(B1-8) methyl acrylate;
(B1-9) alpha-methyl styrene;
(B1-10) dimethylstyrene;
(B1-11) methylstyrene;
(B1-12) vinylbiphenyl;
(B1-13) glycidyl acrylate;
(B1-14) glycidyl methacrylate;
(B1-15) glycidyl propylene;
(B1-16) 2-methyl-2-vinyl oxirane;
(B1-17) vinyl pyrridine;
(B1-18) aminoethyl methacrylate; and
(B1-19) aminoethylphenyl acrylate.

[0058] Another preferred embodiment of formula (B) is the following general structure (B2):



(B2)

where

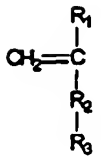
R_{14} and R_{15} are independently selected from H, halogen, alkyl, aryl, substituted alkyl and aryl; alternatively, R_{14} and R_{15} are in the form of a closed ring; and
R_{16} is H, halogen, alkyl, aryl, substituted alkyl or aryl, or unsaturated alkyl.

[0059] Examples for formula (B2) include, but are not limited to:

(B2-1) maleimide;
(B2-2) N-phenyl maleimide;
(B2-3) N-hexyl maleimide;
(B2-4) N-vinylphthalimide; and
(B2-5) N-vinyl maleimide.

[0060] As stated above, the C moiety is a hydrophilic component. The C moiety is selected from a wide variety of monomers such as poly(ethylene glycol) units having general formula (C1), vinyl pyrrolidones having general formula (C2), vinyl imidazoles having general formula (C3) and acrylamides having general formula (C4), all of which polymerize to form water-soluble polymers.

[0061] The general structure of formula (C1) is



(C1)

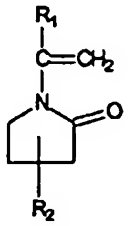
where

R_1 = H, halogen, alkyl, aryl, or substituted alkyl or aryl;
R_2 = direct bond, O, CO, NH, COO, or CONH;
R_3 = OH, $(CH_2CH_2O)_yR_4$, $(CH_2CH(CH_3)O)_yR_4$, or $(CH_2CH(C_2H_5)O)_yR_4$ or the thioether analogs: SH, $(CH_2CH_2S)_yR_4$, $(CH_2CH(CH_3)S)_yR_4$, or $(CH_2CH(C_2H_5)S)_yR_4$;
y = 1 to 200; and
R_4 = alkyl, aryl, substituted alkyl or aryl.

[0062] Examples for general structure (C1) include, but are not limited to:

(C1-1) poly(ethylene glycol) methyl ether acrylate of average molecular weight 404;
(C1-2) poly(ethylene glycol) methyl ether methacrylate of average molecular weight 418;
(C1-3) poly(ethylene glycol) methyl ether methacrylate of average molecular weight 2068;
(C1-4) poly(ethylene glycol) methyl ether acrylate of average molecular weight 2054; and
(C1-5) polyvinyl alcohol.

[0063] The general structure of formula (C2) is



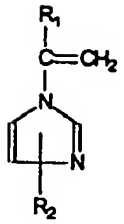
(C2)

where R_1 and R_2 are independently selected from -H, halogen, alkyl, aryl, and substituted alkyl and aryl.

[0064] Examples for general structure (C2) include, but are not limited to:

(C2-1) vinyl pyrrolidone;
(C2-2) vinyl 4-methylpyrrolidone; and
(C2-3) vinyl 4-phenylpyrrolidone.

[0065] The general structure of formula (C3) is



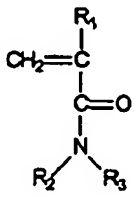
(C3)

where R_1 and R_2 are independently selected from H, halogen, alkyl, aryl, and substituted alkyl and aryl.

[0066] Examples for general structure (C3) include, but are not limited to:

(C3-1) vinyl imidazole;
(C3-2) vinyl 4-methylimidazole; and
(C3-3) vinyl 4-phenylimidazole.

[0067] The general structure of formula (C4) is



(C4)

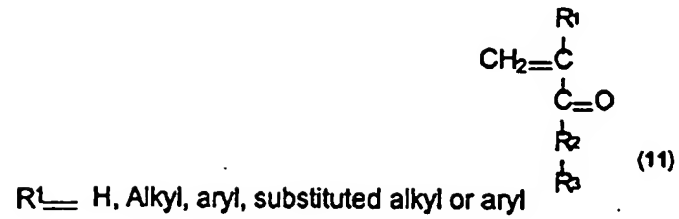
where

R_1 is H, halogen, alkyl, aryl or substituted alkyl or aryl; and
R_2 and R_3 are independently selected from H, alkyl, aryl and substituted alkyl and aryl; alternatively, R_2 and R_3 can form a ring, either aliphatic or aromatic.

[0068] Examples for the general structure (C4) include, but are not limited to:

(C4-1) acrylamide;
(C4-2) methacrylamide;
(C4-3) N,N-dimethyl acrylamide;
(C4-4) N-methyl acrylamide;
(C4-5) N-methyl methacrylamide;
(C4-6) aryloxy piperidine; and
(C4-7) N,N-diethyl acrylamide.

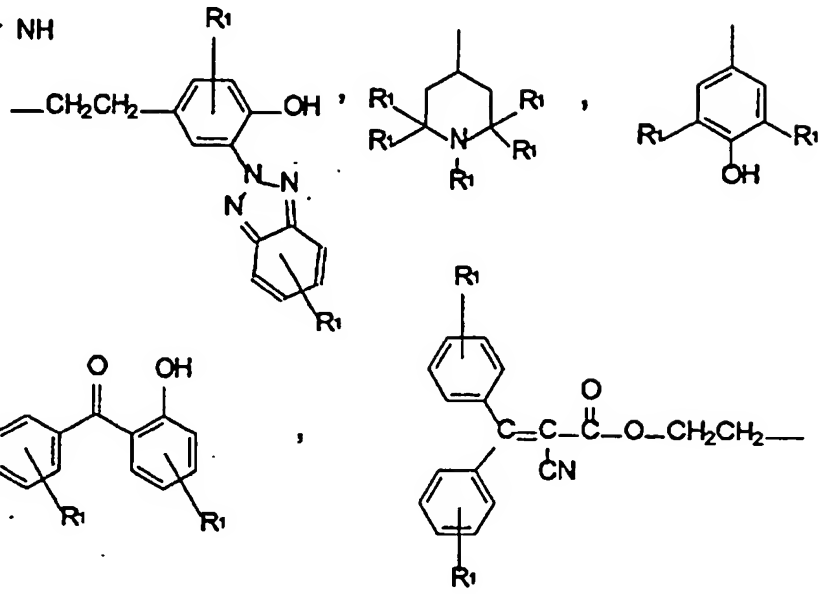
[0069] As stated above, the *D* moiety is a UV absorber composed of monomer(s) having the general structure of formula (D)



(11)

R^1= H, Alkyl, aryl, substituted alkyl or aryl

R^2= O or NH

R^3= 

[0070] As stated above, the *E* moiety is a highly polar functional group composed of moieties having the general structure given by formulae (E1) to (E10).

[0071] The general structure of formula (E1) is

$$CH(R_1) = C(R_2)R_3COOH \qquad (E1)$$

where

R_1 =H, COOH, $COOR_4$;
R_2 = H, halogen, alkyl, aryl, alkoxyl, or substituted alkyl, aryl or alkoxyl;
R_3 = direct bond, alkylene, arylene or sustituted alkylene or arylene; and
R_4 = alkyl, aryl, substituted alkyl or aryl.

[0072] Examples for structure (E1) include, but are not limited to:

(E1-1) acrylic acid;
(E1-2) methacrylic acid;
(E1-3) chloromethacrylic acid;

(E1-4) maleic acid; and
(E1-5) vinyl benzoic acid.

[0073] The general structure of formula (E2) is

$$CH_2 = CHR_1NR_2R_3 \quad (E2)$$

where

R_1 = alkylene, arylene, substituted alkylene, arylene, acetals, hemiacetals, -CHO, -COOH, $-CH_2OH$, or $-SO_2$; and R_2 and R_3 are independently selected from H, alkyl, aryl, or substituted alkyl, aryl or alkoxyl; alternatively, R_2 and R_3 can be combined to form a ring, either aliphatic or aromatic.

[0074] Examples for structure (E2) include, but are not limited to:

(E2-1) allylamine;
(E2-2) N,N-diethylallylamine; and
(E2-3) vinyl sulfonamide.

[0075] The general structure of formula (E3) is

$$y\ (CH_2 = CHR_1COO^-)\ M^{y+} \quad (E3)$$

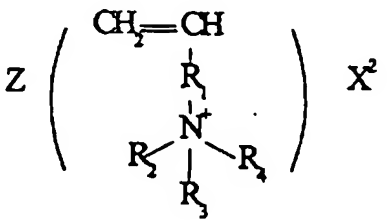
where

R_1 = alkylene, arylene, substituted alkylene or arylene;
y = 1 to 4; and
$M^{y+} = NH_4^+$, Li^+ Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Ti^{4+}, triethylammonium, diethylammonium, pyrridinium, etc.

[0076] Examples for structure (E3) include, but are not limited to:

(E3-1) sodium acrylate;
(E3-2) sodium methacrylate;
(E3-3) ammonium acrylate; and
(E3-4) ammonium methacrylate.

[0077] The general structure of formula (E4) is



(E4)

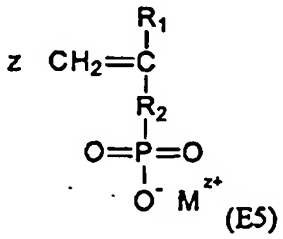
where

R_1 = alkylene, arylene, substituted alkylene or arylene, COO, or cyclic ring containing nitrogen;
R_2, R_3, and R_4 are independently selected from H, alkyl, aryl, alkoxyl, or substituted alkyl, aryl or alkoxyl;
z = 1 to 4; and
X = halogen, BF_4, PF_6, ClO_4, SCN, CNO, CNS.

[0078] Examples for general structure (E4) include, but are not limited to:

(E4-1) acrylamidopropanetriethylammonium chloride;
(E4-2) methacrylamidopropanetriethylammonium chloride; and
(E4-3) vinylpyridine hydrochloride.

[0079] The general structure of formula (E5) is



(E5)

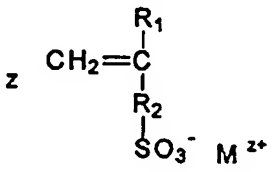
where

R_1 = H, alkyl, aryl, alkoxyl, substituted alkyl, aryl or alkoxyl;
R_2 = direct bond, alkylene, arylene or substituted alkylene or arylene;
z = 1 to 4; and
M^{z+} = NH_4^+, Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Ti^{4+}, triethylammonium, diethylammonium, pyrridinium, etc.

[0080] Examples for the general structure (E5) include, but are not limited to:

(E5-1) sodium vinyl phosphonate; and
(E5-2) sodium 1-methylvinylphosphonate.

[0081] The general structure of formula (E6) is



(E6)

where

R_1 = H, alkyl, aryl, alkoxyl, substituted alkyl, aryl or alkoxyl;
R_2 = direct bond, $-COOR_3$, arylene, alkylene, or $-CONHR_3$;
R_3 = alkylene, arylene, substituted alkylene or arylene, or fluoroalkylene;
z = 1 to 4; and
M^{z+}, = NH_4^+, Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Ti^{4+}, etc.

[0082] Examples for the general structure (E6) include, but are not limited to:

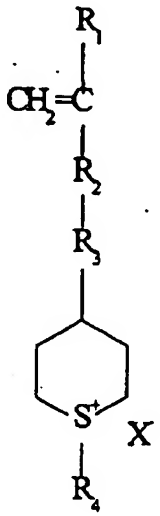
(E6-1) sodium vinyl sulfonate;
(E6-2) sodium 1-methylvinylsulfonate;
(E6-3) sodium styrenesulfonate;
(E6-4) sodium acrylamidopropanesulfonate;

(E6-5) sodium methacrylamidopropanesulfonate; and
(E6-6) sodium vinyl morpholine sulfonate.

[0083] Additional E moieties include the following salts:

(E7) sulfonium salts;
(E8) carbonium salts;
(E9) pyrrilinium salt and thio pyrrilinium salt; and
(E10) tetrazolium salt.

[0084] The sulfonium salts have the following structure (E7):

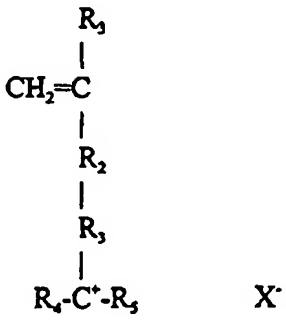


(E7)

where

R_1 = H, halogen, alkyl, or aryl;
R_2 = CO, O;
R_3 = direct bond, NH;
R_4 = alkyl or aryl; and
X = Cl, Br, BF_4, ClO_4, I, or NO_3.

[0085] The carbonium salts have the following structure (E8):

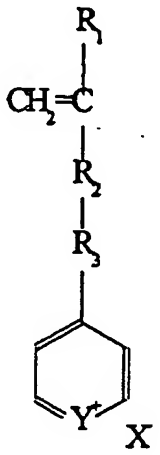


(E8)

where

R_1 = H, halogen, alkyl, or aryl;
R_2 =CO, O;
R_3 = direct bond, NH, alkylene, or arylene;
R_4 and R_5 are independently selected from alkyl or aryl; and
$X = SbF_5^-$, FSO_3^-.

[0086] The pyrrilinium and thiopyrrilinium salts have the following structure (E9):



(E9)

where

Y = O or S;
R_1 = H, halogen, alkyl, or aryl;
R_2 = CO, O;
R_3 = direct bond, NH, alkylene, or arylene;
X = Cl, Br, I, ClO_4, BF_4, etc.

[0087] As stated above, the *F* moiety is a functional group that contains an aldehyde functionality (-CHO), a carboxylic acid functionality (-COOH), or an allyl functionality ($-CH_2OH$).

[0088] Examples for structure (F1) include, but are not limited to:

(F1-1) acrolein;
(F1-2) acrolein dimethyl acetal;
(F1-3) acrolein diethyl acetal;
(F1-4) acrolein ethylene acetal;
(F1-5) allyl alcohol; and
(F1-6) acrylic acid.

[0089] The use of an aldehyde, carboxylic acid, or allyl alcohol in the *F* moiety is based on the reaction of these functional groups with hydroxy groups. For example, the reaction of an aldehyde with an alcohol produces a hemiacetal, which can react with an additional alcohol to produce an acetal, which is more stable than a hemiacetal, and water. Since cellulose has three available hydroxy groups per repeat unit, then the functional group on the *F* moiety will react with the hydroxy groups on the cellulose to bind the core/shell polymer to the cellulose. Since the core/shell binder is associated with the colorant, the colorant is likewise bound to the cellulose. The amine-containing additive apparently serves to catalyze the reaction of the functional group on the *F* moiety with the hydroxy groups on the cellulose.

[0090] More precisely, the colorant is trapped in the matrices of the polymer and the polymer in turn is associated with the cellulosic structure of the media. In the absence of amino compounds, the reaction is slow, but still the same sequence of events occur.

Polymers

[0091] Polymers that fall within the scope of the formula (I) include, but ar not limited to, the following examples:

(1) (hexyl acrylate)$_{20}$ (methyl methacrylate)$_{20}$ (acrylamide)$_{50}$ (acrolein)$_{10}$
(2) (styrene)$_{34}$ (methyl methacrylate)$_{8}$ (vinylpyrrolidone)$_{50}$ (acrolein)$_{8}$
(3) (styrene)$_{20}$ (methyl methacrylate)$_{20}$ (acrylamide)$_{50}$ (acrolein)$_{10}$
(4) (styrene)$_{20}$ (methyl methacrylate)$_{20}$ (acrylamine)$_{50}$ (acrolein dimethyl acetal)$_{10}$
(5) (hexyl acrylate)$_{20}$ (methyl methacrylate)$_{20}$ (poly(ethylene glycol) methyl ether acrylate, mw=404)$_{60}$ (acrolein)$_{10}$
(6) (hexyl acrylate)$_{10}$ (methyl methacrylate)$_{10}$ (poly(ethylene glycol) methyl ether acrylate, mw=404)$_{60}$ (acrolein)$_{20}$
(7) (hexyl acrylate)$_{20}$ (methyl methacrylate)$_{20}$ (acrylamide)$_{50}$ (methacrolein)$_{10}$
(8) (styrene)$_{34}$ (methyl methacrylate)$_{8}$ (vinyl pyrrolidone)$_{50}$ (methacrolein)$_{8}$
(9) (styrene)$_{20}$ (methyl methacrylate)$_{20}$ (arylamide)$_{50}$ (methacrolein)$_{10}$
(10) (hexyl acrylate)$_{20}$ (methyl methacrylate)$_{20}$ (poly(ethylene glycol) methyl ether acrylate, mw=404)$_{60}$ (methacrolein)$_{10}$
(11) (hexyl acrylate)$_{20}$ (methyl methacrylate)$_{20}$ (poly(ethylene glycol) methyl ether acrylate, mw=2054)$_{60}$ (methacrolein)$_{10}$
(12) (hexyl acrylate)$_{20}$ (methyl methacrylate)$_{20}$ (poly(ethylene glycol) methyl ether acrylate, mw=2054)$_{60}$ (acrolein)$_{10}$
(13) (hexyl acrylate)$_{20}$ (methyl methacrylate)$_{20}$ (poly(ethylene glycol) methyl ether acrylate, mw=2054)$_{60}$ (acrolein dimethyl acetal)$_{10}$
(14) (hexyl acrylate)$_{10}$ (methyl methacrylate)$_{10}$ (poly(ethylene glycol) methyl ether acrylate, mw=404)$_{60}$ (methacrolein)$_{20}$
(15) (lauryl methacrylate)$_{43}$ (methyl methacrylate)$_{11}$ (acrylic acid)$_{21}$ (styrene sulfonate, sodium salt)$_{22}$ (methacrolein)$_{3}$
(16) (lauryl methacrylate)$_{43}$ (methyl methacrylate)$_{11}$ (acrylic acid)$_{21}$ (styrene sulfonate, sodium salt)$_{22}$ (acrolein)$_{3}$.

INKS

[0092] Any of the commonly employed colorants in ink-jet printing technology may be used in the practice of the present invention. While dyes, whether water-insoluble or water-soluble, may be employed, the core/shell binder is preferably employed with pigments.

[0093] Without being limited to theory, it is believed that the primer is associated with the colorant in solution and the primer and durable core/shell polymers are encapsulating the colorants upon drying; this appears to be the case after printing the ink on a print medium, such as paper. However, the present invention is meant to include ink formulations which comprise the polymers and colorants without limit to the type of association between the colorant and the polymer.

[0094] The following pigments are useful in the practice of the invention; however, this listing is not intended to limit the invention. The following pigments are available from BASF: Paliogen® Orange, Heliogen® Blue L 6901F, Heliogen® Blue NBD 7010, Heliogen® Blue K 7090, Heliogen® Blue L 7101F, Paliogen® Blue L 6470, Heliogen® Green K 8683, and Heliogen® Green L 9140. The following pigments are available from Cabot: Monarch® 1400, Monarch® 1300, Monarch® 1100, Monarch® 1000, Monarch® 900, Monarch® 880, Monarch® 800, Monarch® 700, Cabojet200, Cabojet300, IJX55, and IJX76. The following pigments are available from Ciba-Geigy: Chromophtal® Yellow 3G, Chromophtal® Yellow GR, Chromophtal® Yellow 8G, Igrazin® Yellow 5GT, Igralite® Rubine 4BL, Monastral® Magenta, Monastral® Scarlet, Monastral® Violet R, Monastral® Red B, and Monastral® Violet Maroon B. The following pigments are available from Columbian: Raven 7000, Raven 5750, Raven 5250, Raven 5000, and Raven 3500. The following pigments are available from Degussa: Color Black FW 200, Color Black FW 2, Color Black FW 2V, Color Black FW 1, Color Black FW 18, Color Black S 160, Color Black S 170, Special Black 6, Special Black 5, Special Black 4A, Special Black 4, Printex U, Printex V, Printex 140U, and Printex 140V. The following pigment is available from, DuPont: Tipure® R-101. The following pigments are available from Heubach: Dalamar® Yellow YT-858-D and Heucophthal® Blue G XBT-583D. The following pigments are available from Hoechst: Permanent Yellow GR, Permanent Yellow G, Permanent Yellow DHG, Permanent Yellow NCG-71, Permanent Yellow GG, Hansa Yellow RA, Hansa Brilliant Yellow 5GX-02, Hansa Yellow-X, Novoperm® Yellow HR, Novoperm® Yellow FGL, Hansa Brilliant Yellow 10GX, Permanent Yellow G3R-01, Hostaperm® Yellow H4G, Hostaperm® Yellow H3G, Hostaperm® Orange GR, Hostaperm® Scarlet GO, and Permanent Rubine F6B. The following pigments are available from Mobay: Quindo® Magenta, Indofast® Brilliant Scarlet, Quindo® Red R6700, Quindo® Red R6713, and Indofast® Violet. The following pigments ar available from Sun Chemical: L74-1357 Yellow, L75-1331 Yellow, L75-2577 Yellow, YGD 9374 Yellow, YHD 9123 Yellow, YCD 9296 Yellow, YFD 1100 Yellow, QHD6040 Magenta, QFD1180 Magenta, RFD3217 Magenta, QFD1146 Magenta, RFD9364

Magenta, QFD 9334 Magenta, BCD6105 Cyan, BCD9448 Cyan, BCD6060 Cyan, BFD5002 Cyan, BFD1121 Cyan, and LHD9303 Black.

[0095] Dyes, whether water-soluble or water-insoluble, may be employed in the practice of the present invention, although not as preferred as pigments. Examples of water-soluble dyes include the sulfonate and carboxylate dyes, specifically, those that are commonly employed in ink-jet printing. Specific examples include: Sulforhodamine B (sulfonate), Acid Blue 113 (sulfonate), Acid Blue 29 (sulfonate), Acid Red 4 (sulfonate), Rose Bengal (carboxylate), Acid Yellow 17 (sulfonate), Acid Yellow 29 (sulfonate), Acid Yellow 42 (sulfonate), Acridine Yellow G (sulfonate), Nitro Blue Tetrazolium Chloride Monohydrate or Nitro BT, Rhodamine 6G, Rhodamine 123, Rhodamine B, Rhodamine B Isocyanate, Safranine O, Azure B, Azure B Eosinate, Basic Blue 47, Basic Blue 66, Thioflacin T (Basic Yellow 1), and Auramine O (Basic Yellow 2), all available from Aldrich Chemical Company. Examples of water-insoluble dyes include azo, xanthene, methine, polymethine, and anthroquinone dyes. Specific examples of water-insoluble dyes include Ciba-Geigy Orasol Blue GN, Ciba-Geigy Orasol Pink, and Ciba-Geigy Orasol Yellow.

[0096] In the event that one or more surfactants are employed in place of hydrophilic groups on the smear-fast core/shell polymer, the concentration of such surfactant(s) is in the range of about 0.001 to 10 wt%, preferably about 0.01 to 5 wt%, of the ink.

1. Additives to Inks to React with Cellulosic Media

[0097] In addition to at least one of the foregoing core/shell polymeric binders, the ink-jet printing inks of the present invention include certain amine-containing additives to the vehicle, which may be characterized as water-soluble and/or water-dispersive amines, polyamines, and amine alcohols. Preferably, amine alcohols are employed in the practice of the present invention.

[0098] The amine alcohols have the general formula (II)

(II)

where R_1 and R_2 are independently selected from the group consisting of hydrogen, alkyl, alkoxy, aryl, and phenoxy, R is alkylene, and X is selected from the group consisting of hydrogen, alkyl, aryl, -OH, -COOH, and -CHO. Examples of amine alcohols employed as additives include ethanolamine, dimethylaminopropanol, aminobutanol and derivatives thereof, dipropylaminopropane diol, amino propane diol, 2(2-ethylethoxyamino ethanol), dimethylaminobutanol, 2-(diisopropylamino)ethanol, diisopropanolamine, hydroxyquinone, 3-(2-hydroxyethylamino)-5,5-dimethyl-2-cyclohexene-1-one, 3-(1-hydroxyethyl)aniline, 4-morpholine ethanol, and 3-morpholino-1,2-propanediol.

[0099] In the situation in which polymer (I') is employed, X is preferably hydrogen.

[0100] Amines without the alcohol group may also be employed in the practice of the present invention, as well as polyamines and polyamino alchohols.

[0101] Examples of water-soluble and/or water-dispersive amines, preferably water-soluble amines, include 1, 4-bis(3-aminopropyl) piperazine (Aldrich Cat. # 10,943-6), dimethylamine (Aldrich Cat. # 38,824-6), 1-methylimidazole (Aldrich Cat. # 33,609-2), ethylenediamine (Aldrich Cat. # 39,108-5), piperidine (Aldrich Cat. # 10,409-4), piperazine (Aldrich Cat. # P4,5907), 1-piperidineethanol (Aldrich Cat. # 11,606-8), 2-piperidineethanool (Aldrich Cat. # 43,359-4), 3-piperidinemethanol (Aldrich Cat. # 15,522-3), and 2-piperidinemethanol (Aldrich Cat. # 15,522-5).

[0102] An example of a suitable polyamine is oxazoline functional polymer emulsion, available from Nippon Shakubai under the trade designation EPOCROS K1000. Examples of additional polyamines include poly (dimethylamine-co-epichlorohydrin) (Aldrich Cat. # 40,911-1), poly (diallyldimethylammonium chloride) (Aldrich Cat. # 40,902-2), poly ethyleneimine (Aldrich Cat. # 40,871-9), poly ethyleneimine (Aldrich Cat. # 40,870-0), poly ethyleneimine (Aldrich Cat. # 40,872-7), poly ethyleneimine (Aldrich Cat. # 18,197-8), poly ethyleneimine ethoxylated (Aldrich Cat. # 30,618-5 & 42347-5), Jeffamines (emulsion polyamines available from Zeneca), and poly dimethylaminoacrylate (Poly Science).

[0103] The above-described amine-containing additives serve to raise pH and control printability of the ink. The concentration of the amine-containing additive is within the range of about 0.005 to 50 wt%, preferably about 0.01 to 10 wt%, of the ink composition.

[0104] In the ink compositions of the present invention, the ratio of colorant (pigment) to binder (I) is between 10:1 and 1:10, preferably between 5:1 and 1:5, and most preferably between 3:1 and 1:3.

[0105] The general ink formulation comprises: